THE HALL EFFECT IN THIN
TITANIUM, NIOBIUM, TANTALUM, AND PALLADIUM
LAYERS CONTAINING INTERSTITIAL HYDROGEN

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Dedicated to the 65th anniversary of the late Academician R. Brdička.

Results of the measurements of the Hall coefficient changes in thin titanium, niobium, tantalum, and palladium layers during the hydrogen sorption by these metals are presented. The results have been discussed on the basis of the phenomenological model of two overlapping bands. In order to achieve a qualitative agreement of predicted and experimentally found changes, it is necessary to assume that hydrogen in the form of protons is present in the metal. The results show that the rigid-band model may be used in the first approximation to explain the Hall coefficient changes in titanium–hydrogen and niobium–hydrogen systems. On the basis of the measured data no conclusion can be drawn as to the applicability of this model to the palladium–hydrogen system.

The metals of the third and fourth groups of the periodical system absorb hydrogen considerably and produce solid solutions having nonstoichiometric composition and metallic conductivity[1-3]. Palladium[4] exhibits a similar behaviour. The problem of the chemical hydrogen bond in the above-mentioned metals has not been hitherto quite satisfactory explained, in spite of the considerable advance made with use of the methods such as NMR, X-ray and neutron diffraction. There are three possible models of the hydrogen bond[1]: *1.* hydrogen is present as protons and its electrons become a part of the collectivized system of the metal electrons, *2.* hydrogen is bound covalently, *3.* hydrogen in the metal is present in the form of anions. The problem of the hydrogen bond in transition metals is likewise significant in view of their application as hydrogenation catalysts. A slow dissolution of hydrogen in the metal occurs within the catalytic reaction, hence the electron structure of the metal changes, thus the catalytic activity and selectivity of the metal being changed.

The fact that during the dissolution of hydrogen in transition metals a change in the values of their collective electronic characteristics (specific resistivity, electronic specific heat, paramagnetic susceptibility *etc.*) takes place, is well-known[1-4]. From the extent and course of these changes a conclusion as to the character of the hydrogen bond in the metal may be drawn, but it is usually uneasy and not unambiguous to interpret the data found. Obviously, the use of other experimental methods can be of assistance in the interpretation of the data that have been obtained up to now.

In the present paper, the results of the measurements of the Hall voltage changes in thin titanium, niobium, tantalum, and palladium layers (films) during the hydrogen

sorption are given. By maintaining suitable experimental conditions[5], these changes are primarily caused by changes in value of the Hall coefficient which is very sensitive to the solid phase electronic structure.

When discussing classical transport effects in the transition metals, the two-band model has been most frequently used[6,7]. Within the framework of this model, the Hall coefficient in the approximation of independent bands is given by

$$R_H = \frac{e^3}{12\pi^3 hc}\left(\frac{1}{\sigma^2}\right)(\beta_e + \beta_h);$$

$$\beta = l\langle A\rangle \tau/\langle m^*\rangle, \qquad (1)$$

where l is the mean free path of current carriers in the metal, $\langle A\rangle$ is the effective Fermi surface area, τ is the relaxation time and $\langle m^*\rangle$ is the average value of the effective mass of conduction electrons, e the electron charge, π the Ludolphian number, h the Dirac constant, and c the velocity of light in vacuum. The subscripts e and h denote that carriers with the positive (electrons) or negative ("holes") effective mass are concerned, σ is the conductivity. In the approximation of free electrons, equation (1) can be put to the known form

$$R_H = \frac{1}{|e|c}\frac{n_h\mu_h^2 - n_e\mu_e^2}{(n_h\mu_h + n_e\mu_e)^2}, \qquad (2)$$

where n and μ is the density and mobility of corresponding current carriers, respectively. With thin layers, the thickness of which is comparable to the mean free path of the current carriers in the metal, the Hall coefficient is a function of the layer thickness (it increases with the decreasing thickness) and its value is also dependent on character of the interaction of the carriers with a potential barrier at the metal surface[8,9]. The alterations of these effects during the hydrogen sorption, which is a volume process, can be in most cases neglected, when compared with changes in the volume electronic structure.

EXPERIMENTAL

The experimental arrangement did not differ substantially from that described previously[5,10]. Thin layers 300—600 Å thick (determined by chemical analysis and from the layer transparency) were prepared by evaporating the metal from a resistively heated filament (filament diameter of 0·3 mm) and by deposition of the metal on a tempered (200°K) support made of hard glass (Sial). The total pressure of residual gases in the apparatus did not exceed 10^{-8} Torr during vapour-deposition of the metal. The direct current method and magnetic fields up to 4 kG were used for the Hall voltage measurements. The measuring device allows to record changes of the order of magnitude 10^{-8} V with great reliability. The following purity of metals was taken use of:

titanium 99·3%, niobium 99·98%, tantalum 99·5%, palladium 99·99%. Furthermore, electrolytically pure hydrogen was purified by diffusion trough a palladium thimble[11]. The measurements were carried out with titanium, niobium, and tantalum at a temperature of 273°K, with palladium at 80°K (sorption of hydrogen from the gas phase by palladium proceeds very slowly at 273°K).

RESULTS

Relative values of the Hall coefficient changes $\Delta R_H/R_{Ho}$ as dependent on the value of atomic ratio H/Me are for the studied systems summarized in Fig. 1. The measurements were carried out up to a maximum value of the hydrogen stationary pressure p of 10^{-2} Torr over the sorbent. Accurate values of the H/Me ratio could not be determined for the given experimental arrangement, because of the fact that likewise sorption of hydrogen by the metal deposited on internal sides of the measuring cell, and sorption by the remaining nonevaporated filament are involved. For that reason, data on the values of the atomic H/Me ratios under a stationary hydrogen pressure of 10^{-2} Torr for individual metals were taken from the literature[1-4,12-16]. At the same time, primarily those data were used which were obtained under conditions as close as possible (or identical) to those used in this paper. Because of the hydrogen quantities admitted in individual doses into the measuring cell space being identical
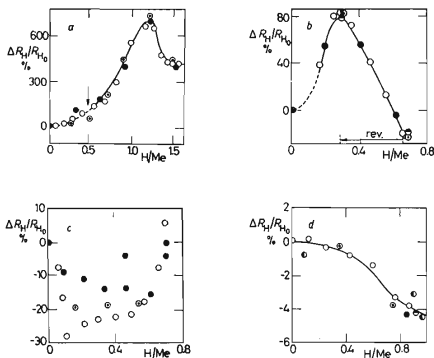

Fig. 1

The Relative Change of the Hall Coefficient Value $K = \Delta R_H/R_{Ho}(\%)$ as a Function of Atomic Ratio $r = $ H/Me of Hydrogen to the Particular Metal During the Hydrogen Sorption by Thin Titanium (*a*), Niobium (*b*), Tantalum (*c*), and Palladium (*d*) Layers

An arrow denotes a point on the curve for the Ti–H₂ system, in which change in the conductivity type occurs; region of the reversible hydrogen sorption is denoted for the dependence in the system Nb–H₂.

within each measurement (with the exception of two or three last gas portions all the admitted hydrogen was sorbed), an approximate linear scale of the H/Me ratios (Fig. 1) could be constructed when knowing the final H/Me value attained in the last portion. Let us mention that the geometry of the employed measuring cell does not lead to a preferential sorption of hydrogen on some places of the cell.

In addition, the changes in electrical resistance of the metal layer were always followed during the sorption and for system Ti–H_2 and Pd–H_2, they were compared with curves of the dependence of the electric resistance upon the sorbed quantity, given in the literature and achieved under equal experimental conditions[12,13]. These comparisons showed that values of the H/Me ratios, graphically presented in Fig. 1, are realistic. Finally, let us mention that the present paper aims at finding a qualitative character of the Hall coefficient changes and possible uncertainties of determining the value of the H/Me ratios do not lead to considerable changes in the given interpretation of the results.

Titanium. Pure titanium films exhibit the n-type conductivity $(R_H < 0)$ and absolute value of the Hall coefficient during the hydrogen sorption decreases at the outset. After the H/Ti ratio has attained a value of approximately 0·5, the conductivity type is changed from n to p, further increase of the sorbed amount results in the rise of the Hall coefficient value and the latter passes through a maximum (H/Ti ≃ 1·2 to 1·3), and finally, it decreases. The sorption is practically irreversible, *i.e.* after pumping off the gas phase, no changes in the Hall coefficient value take place. The establishing of the stationary state after admitting hydrogen is finished within several minutes. The changes found in the electrical resistance of the film during the sorption are analogous to the Suhrmann data[12].

Niobium. For all the studied films $R_H > 0$. The Hall coefficient value rises during the sorption, for the atomic H/Nb ratio of approximately 0·3 it attains a maximum and decreases with further increase of the interstitial hydrogen content in the metal, as far as the value below that measured on a pure niobium film has been reached. After attaining the maximum value of the Hall coefficient, the sorption is reversible. The establishing of the stationary state takes several minutes, similarly as in the Ti–H_2 system. The electrical film resistance increases rapidly at the beginning, and more slowly in the region after attaining the maximum of the R_H coefficient value.

Tantalum. The results presented in this paper for the Ta–H_2 system must be, owing to a bad reproducibility, considered rather orientational. The reason is a very slow establishing of the stationary Hall voltage value and electrical film resistance, which takes several hours. In view of the fact that the measured Hall voltages are very small with the tantalum films (several μV, the magnetic field induction B being 4kG), it is difficult to maintain stability of the whole measuring system with sufficient precision for a period of several hours. Let us mention that the found low rate of sorbing hydrogen by tantalum is in accordance with the literature data[2].

Palladium. For all the studied palladium films $R_H < 0$. The p-type conductivity reported by Ptušinskij[17] for small film thicknesses has not been found for films having metallic conductivity. The changes in the Hall voltage values during the sorption are little (approximately -4% at the saturation with hydrogen). The results of our measurements are in this respect the same as the data given in the literature and obtained for palladium foils electrolytically charged with hydrogen at the temperature of $297°K$[18]. Likewise, the established changes in the electrical film resistance are practically consistent with the literature data[19]. The establishing of the stationary state at the temperature of $80°K$ takes place almost immediately.

DISCUSSION

In order to give a correct interpretation of the Hall coefficient value and its change during the formation of solid solutions and alloys, it would be necessary to start from the band calculation or from the data on the topology of the Fermi surfaces (FS) of the above-mentioned systems which, however, are not available at present time. In addition, the FS of pure transition metals are highly anisotropic which means that the whole "spectrum" of current carriers, having different effective mass values, takes part in the conduction process.

Dissolution of hydrogen in the transition metals usually results in the expansion of the metal crystal lattice and phase transition, in the $Ti–H_2$ system at higher concentrations, antiferromagnetism appears[1-4]. All these changes lead to considerable changes in the FS topology, thus bringing down possibilities to interpret changes in the transport coefficients in terms of the FS. A further complicating factor is anisotropy of the relaxation time, whose influence, on the basis of equation (*1*), may be in the best case respected by introducing a semiempirical correction coefficient. Another possibility which is sufficient for rough qualitative discussions may be seen in the application of diagrams expressing dependence of the state densities upon energy for individual energy bands in connection with equation (*2*).
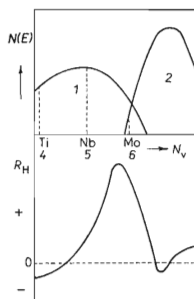
Fig. 2

Behaviour of the Hall Coefficient in the Phenomenological Model of Two Overlapping Bands

Assumed positions of the Fermi levels for Ti, Nb, and Mo are denoted (N_v is the number of valence electrons per metal atom, $N(E)$ is the density of states).

Assuming that each hydrogen atom is a donor (or acceptor) of one electron which enters into the collectivized system of the metal electrons, then the behaviour of the Hall coefficient can be derived from the known shape of the bands, and on the contrary, from the found changes in the value of this coefficient the shape of bands can be suggested and compared with the literature data. This procedure assumes the validity of the so-called rigid-band model[20] for the systems under discussion, *i.e.* we assume that dissolution of hydrogen in the metal changes merely position of the Fermi level, the width and shape of bands being unchanged.

The behaviour of the R_H coefficient in a model of two overlapping bands (Fig. 2) corresponds to that of this coefficient in the systems $Ti-H_2$ and $Nb-H_2$. The shift of the Fermi level towards higher energy values, due to a transport of electrons in the direction Me ← H, will, according to the suggested model, result in the same course of the Hall constant changes as has been that found experimentally. Analogous changes in the Hall constant value have been found[21] for the titanium–molybdenum alloy, *i.e.* change in the conductivity type for $N_v \approx 4.5$ (N_v is a formal number of valence electrons corresponding to one atom of the metal) and existence of a maximum in the p-conductivity region. This analogy gives evidence in favour of the suggested proton model. In the $Ti-H_2$ system, position of the maximum of the Hall constant value is shifted towards lower N_v values than would be expected on the basis of the model presented in Fig. 2 and than has been found for the Ti–Mo alloy ($N_v \approx 5.6$). There are two possible reasons for this difference: *1.* with higher hydrogen content in the metal, expansion of the crystal lattice takes place, which leads to an increase of the effective film thickness and thus to the decrease of the R_H coefficient value, *2.* a change in the width and shape of the bands takes place. The first of the explanations presented is favoured by the fact that the electrical film resistance decreases in this region, in contrast to the behaviour of the massive titanium, where merely its increase takes place[1].

Let us mention that the suggested band model (Fig. 2) is in accord with the curve illustrating total density of states for the transition metals lying at the beginning of periods in the periodic system, the curve being achieved from the electronic specific heat and paramagnetic susceptibilities data[20]. Antiferromagnetism produced in the system $Ti-H_2$ and reported in the literature[2,3] does not follow from the model immediately. These changes are obviously associated with the lattice expansion and phase transition. Corresponding changes in the electronic structure (for example, deformation of bands due to the Jahn-Teller effect[22]) cannot be explained on the basis of the RBM used above. In contrast to the qualitative discussion of the changes in the Hall coefficient value, it will be necessary to use more perfect models to discuss these effects.

As evident from Fig. 2, the suggested model may be also applied to the explanation of changes in the Hall constant value for the $Nb-H_2$ system. In this case, the model qualitatively explains even changes in the electrical resistance and paramagnetic

susceptibility, this being probably due to the fact that only small expansion and distortion of the metal crystal lattice[23] take place during the sorption. For the Nb–H_2 system, the given explanation is likewise in accordance[5] with the expected changes in the FS topology. It follows from a complete calculation of the band structure[5,24] that increase of the Fermi energy will produce reduction of all FS parts and thus the increase of the R_H constant value. At $N_v \approx 5.3$, the central hole part of the FS in the first zone disappears and a new part of the FS having electronic character is produced, this resulting in a decrease of the Hall constant value. By identifying the FS parts with the bands, we obtain the above-mentioned phenomenological model of two overlapping bands. Formation of the FS part of the n-type character then corresponds to the entering of the Fermi level in the band 2 (Fig. 2). The explanation gives only roughly a true picture of the real relations because of a lack of information to what extent individual parts of the FS contribute to the total Hall coefficient value, and because of the uncertainty concerning strength of the spin-orbital splitting which leads to removal of the degeneration of the d-state having symmetry Γ_{25} and thus to changes in the topology of the central FS parts.

We can then summarize that in spite of some complications which would make difficulties in the attempts to give a quantitative interpretation, the measured Hall coefficient values can be explained on the basis of a phenomenological model of two overlapping bands, provided that hydrogen is protonized in the metal and the RBM is valid. Contemporary data on the electronic structure of niobium do not contradict the given explanation.

Similar changes as with the Nb–H_2 system would be expected with the Ta–H_2 system, since the electronic structure of both metals or topology of their Fermi surfaces are probably similar. A qualitative difference of the established changes in the Hall constant (increase in the Nb–H_2 system at the beginning of the hydrogen sorption in contrast to the decrease in the Ta–H_2 system) is therefore surprising. Because of a bad reproducibility of experimental data, due to the reasons mentioned in this paper earlier, it is impossible to decide reliably on the causes of the differences presented. The possibility cannot be excluded that the data given for the Ta–H_2 system in Fig. 1 do not represent the stationary data.

Most of the data reported in the literature for the Pd–H_2 system could be explained[4,25] on the basis of a conception according to which the hydrogen electrons fill up d-band of the metal (screening of produced protons by the electrons of d-band having high density of states is energetically more favourable than screening by electrons of the s-band). Disappearance of paramagnetism after attaining the atomic H/Pd ratio of approximately 0.6 indicated that the palladium d-band contains 0.6 holes per one atom. This opinion was supported also by further experimental data according to which similar changes in the paramagnetic susceptibility take place in the formation of the Pd–Ag alloy, whereas tin, being donor of four electrons, is four times more effective than hydrogen[25]. However, recent measurements of the

de Hass–van Alphen effect on palladium[26] have shown that the metal contains only 0·36 holes/atom; this fact led to the necessity to assume that the hydrogen electrons fill up simultaneously the palladium s and d bands[27].

The changes in the Hall coefficient value during the hydrogen sorption should be analogous with the changes in the value of this constant for the Ag–Pd alloy (similarly as in the Ti–H_2 and Ti–Ho systems), provided that the RBM is valid. However, the behaviour of the Hall constant of both mentioned systems differ; with the Ag–Pd alloy, absolute value of the Hall coefficient rises with the increasing silver content, attains a maximum for 40% Ag, and afterwards, it decreases[28]. The difference in the behaviour of the R_H coefficient in both systems is likely due to a different mechanism of the current carrier scattering, because the Ag–Pd system is a substitutional alloy, while for the Pd–H_2 system, the assumed protons are present in interstitial (at 80°K probably primarily octahedral[1,4,19]) positions of the metal crystal lattice. This means that application of the RBM to the Pd–H_2 system does not enable a satisfactory explanation of the measured data.

With palladium, the electrical current is transferred mostly by s-electrons, since it holds, as a consequence of high state densities in the d-band, that $\mu_e \gg \mu_h$. Analysis of equation (2) shows that in this case, even a considerable decrease in the mobility of s-electrons will result in a small decrease of the absolute value of the Hall constant, and hence the measured changes in the R_H coefficient may be explained. Likewise, changes in anisotropy of the effective mass and relaxation time may operate[5].

Let us mention that in the case of palladium, exchange interactions[29,30] are responsible for a high value of the paramagnetic susceptibility. A question therefore arises, whether a similar expression as for ferromagnetics should not be used for the Hall voltage. The quantum mechanical treatment shows[31] that the effective value of the Hall constant is then given, provided that the FS does not differ too much from the spherical one, by the expression

$$R_h^* = R_0 + b\varrho^2\chi, \qquad (3)$$

where R_0 is the classical Hall coefficient given by equation (1), b is the constant, ϱ denotes the resistivity, and χ is the paramagnetic susceptibility. Equation (3) may be successfully applied[5] to the explanation of the temperature dependence of the Hall coefficient for palladium, the application to the Pd–H_2 system, however, will require a more detailed theoretical study.

The established changes in the Hall coefficient value for the Pd–H_2 system do not then exclude the proton model, but they do not confirm it unambiguously either.

The results of the made measurements have shown usefulness of the study of galvanomagnetic effects in nonstoichiometric hydrides of the transition metals, particularly in connection with elucidation of the problem of the hydrogen bond in these metals. Use of thin polycrystalline films brings some difficulties in the interpretation

of the data; however, they are balanced by the possibility of preparing very pure metallic sorbents and simplicity of their sorption with hydrogen, which can be carried out under exactly defined conditions.

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